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(71)Applicant : HITACHI LTD
(72)Inventor : NAKATSUKA TETSUYA
SOGA TASAO
SHIMOKAWA HIDEYOSHI
YAMAMOTO KENICHI
HARADA MASAHIDE
OCHIAI YUJI
KAMEI TSUNEAKI

(54) LEAD-FREE SOLDER AND PACKAGING METHOD USING THE SAME AND PACKAGED ARTICLES

(57)Abstract:
PROBLEM TO BE SOLVED: To make it possible to execute lead-free soldering within the heat resistant temp. of a glass epoxy substrate by using lead-free solder specified in the contents of ZnBi and Sn.
SOLUTION: The lead-free solder is composedby mass %of <4 to 5% Zn13 to 16% Bi and the balance Sn. The org. insulating substrate is printed with such Zn-Bi-Sn solder paste and the solder paste is melted at the heat resistant temp. of the org. insulating substrate or belowby which the org. insulating substrate and its mounting parts are connected. The glass epoxy substrateetc.are used for the org. insulating substrate and electronic parts are packaged thereon. This lead-free solder is used for BGA packages or as ballsetc.for chip carriers. The lead-free solder ensures reflow at about ≤220° C. The reflow at ≥150° C is warranted. The reflow by assuring the sufficient wettability on Cu conductors with a weak flux or with the Sn solder plated terminal constitution of parts is

made possible. This solder is substitutive for Sn-Pb eutectic solder.

CLAIMS

[Claim(s)]
[Claim 1]Lead-free soldering having made less than [more than 4mass%5mass%] and Bi less than more than 13mass%16mass%and setting the remainder to Sn for Zn in solder which consists of Zn-Bi-Sn.
[Claim 2]In a board mounting method using lead-free solder which consists of Zn-Bi-SnSoldering paste which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass%16mass%and set the remainder to Sn by printing to an organic insulating substrate. A board mounting method using lead-free soldering melting said soldering paste below at heat-resistant temperature of said organic insulating substrateand connecting said organic insulating substrate and its mounted part.
[Claim 3]In a board mounting method using lead-free solder which consists of Zn-Bi-SnFor Zn less than more than 4mass%6mass% and Bi Less than more than 13mass%16mass%. A board mounting method using lead-free soldering melting below at heat-resistant temperature of said organic insulating substrate using solder which consists of Zn-Bi-Sn which set the remainder to Snand connecting said organic insulating substrate and its mounted part.
[Claim 4]Zn for an organic insulating substratea mounted part carried in said organic insulating substrateand said organic insulating substrate and said mounted part Less than more than 4mass%6mass%. A mounting article by lead-free soldering connection connecting with solder which consists of Zn-Bi-Sn which made Bi less than more than 13mass%16mass%and set the remainder to Sn.
[Claim 5]a weight (mass) % display of a presentation [in / on soldering of an organic insulating substrateand / Zn-Bi-Sn3 element system] -- coordinates (Zn.) Lead-free soldering for organic insulating-substrate connection using alloy solder of a presentation which displays by Bi and Snis surrounded by A (616**)B (613**)C (5.512**)D (4.514**)and E (3.716**)and changes.
[Claim 6]A board mounting method and a mounting article using lead-free soldering characterized by said organic insulating substrate being a glass epoxy board in claim 2 thru/or claim 5and lead-free soldering.
[Claim 7]A board mounting method and a mounting article using lead-free soldering using AgCuSb or Inor its combination as an additive of said

lead-free soldering further in claim 1 thru/or claim 6and lead-free soldering.
[Claim 8]A board mounting method and a mounting article using lead-free soldering using said lead-free soldering in claim 1 thru/or claim 7 as a ball for a BGA (Ball Grid Array) package or for chip carriersand lead-free soldering.
[Claim 9]In claim 1 thru/or claim 8a terminal is supplied for said lead-free soldering with a wire bondA board mounting method and a mounting article using lead-free soldering filling up between a chip and a substrate with resin of 500 to 1000 kgf/mm Young's modulus ^{2}and coefficient-of-thermal-expansion 15x10^{-6}/** - 35x10^{-6}/**and lead-free soldering.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]In order that this invention may connect LSIpartsetc. to a glass epoxy boardSoldering in the maximum temperature of 220 ** is possibleand it is related with the soldered-joint method using the Sn-Zn-Bi system lead-free soldering which guarantees the connection reliability under the elevated temperature in 150 **and itand the mounting article using it.
[0002]
[Description of the Prior Art]The printed circuit board construction material currently generally used is a product made from glass epoxy. The heat-resistant temperature of a glass epoxy board is usually 220 **when a reflow furnace is used. As a presentation of the solder for connection used for thisthe thing Sn-37mass%Pb eutectic crystal solder (melting point: 183 **) or near the eutectic crystal was common. from it being around 183 **these melting points can make connection sufficient at below the heat-resistant temperature (220 **) of the glass epoxy board currently used widelyand guarantee a maximum of 150 ** of the reliability -- things were able to be carried out.
[0003]If the printed circuit board currently used for electronic parts in the U.S. is neglected by carrying out ** commonthe lead (it is hereafter described as Pb) contained in this solder reacts to acid easilyand melts into groundwater (acid rain is also accelerated) and it is used for drinking water these dayshaving an adverse effect on a human body is announced officiallyand it has been a problem. Thenas a Pb free

solder replaced with Sn-Pb system solderthere is little influence on environmentthere is little toxicity to a human bodythere are few problems of exhaustion of resourcesthere are also few problems in a cost aspectand a close-up of Sn with the operating experience as a materialZnand Bietc. is taken as a major candidate. With 2 element-system solderSn-3.5mass%Ag (melting point of 221 **) and Sn-5mass%Sb (melting point of 240 **) already have an operating experience as Pb free solder.
[0004]Howeversince these solder has too high the melting point compared with Sn-Pb eutectic crystal solderit cannot secure connection sufficient at below the heat-resistant temperature (220 **) of a glass epoxy boardand cannot use it for the soldering.
[0005]As other solder materialsalthough there is Sn-9mass%Zn (eutectic crystal with a melting point of 199 **)such the melting point is low that this can also carry out a reflow of the electronic parts at 220 ** which is the heat-resistant temperature of a glass epoxy board. Even if it uses the flux (chlorine 0.2mass% content) of a rosin system currently generally usedit turns out that it can hardly apply in the reflow temperature of 220 **. Since the quantity of this solder material of Zn increasesthe surface will oxidize easily remarkably and the wettability over Cu or nickel will fall remarkably compared with a Sn-Ag system and a Sn-Sb system.
[0006]In an old track recordalthough one high 30-50 ** is experientially known to the melting point of solder as for soldering temperaturewhen wettability is badthis temperature gradient becomes large further.
[0007]Although there are Sn-Bi system solder (representation presentation Sn-58mass%Bi; melting point of 138 **) and Sn-In system solder (representation presentation Sn-52mass%In; melting point of 117 **) other than thesethese cannot guarantee high temperature strength of 150 **when solidus temperature falls -- Sn-37mass% -- it cannot be said to be the solder for Pb eutectic crystal solder substitution.
[0008]Although the 4 element-system Pb free solder material of Sn-2%Ag-7.5%Bi-0.5%Cu (liquidus temperature: 211 **solidus temperature:183 **) is also proposed by the Sn-Ag systemsince the melting point is still higha reflow within the heat-resistant temperature of a glass epoxy board is difficult too. Plural systemstherefore ingredient control are difficult. In thermometric analysisif the solidus line of the low temperature of a 130 ** level is detected slightly and lowers liquidus temperature:211 ** furtherthe solidus temperature of 130 ** low temperature will appear clearly.
[0009]That isexcept the Sn-Zn systemthe solder material in which a 220

** reflow is possible is not found out without having the low-temperature solidus line.
[0010]A Sn-Zn-In system and a Sn-Zn-Bi system are among the solder materials which avoid this problem as the main ingredients. It decided to examine this time three element systems of a Sn-Zn-Bi system which is the combination of an element with an operating experience in consideration of the fall of the life time by a reaction with costtoxicitycorrosion resistanceand weatherproof fluxetc. This solder is considered to be promising also from the field of the melting point besides the above-mentioned evaluation criteria.
[0011]Drawing 1 is a publicly known constitutional diagram of 3 element-system solder of Sn-Zn-Bi. It is by International Crit-ical Tablesand [2 (1927)418]. Although the temperature distribution of the whole rough melting point (liquidus temperature) is knownit is the actual condition which detailed distributiona clear temperatureetc. do not understand. That isthe relation of the liquidus temperature and solidus temperature which are needed here is unknown. A dotted line is a 2 yuan eutectic crystal line. Other solid lines show the isothermal line of each temperature.
[0012]About Sn-Zn-Bi system solderJP57-11793A and JP59-189096A have a statement.
[0013]In JP57-11793Athe solder for low melting point aluminum excellent in the corrosion resistance which 5 - 10mass% becomes in Znand the remainder becomes from Sn 8 - 13mass% in Bi is proposed. This is not aimed at connection with the printed circuit board which consists of a Cu conductor for the purpose of the improving strength in the solder for aluminum. As a reason for having decided the range of this Zn (5 - 10mass%) and Bi (8 - 13 mass%)in the case of Znsoldering insufficient strength with aluminum is pointed out and 7 - 9mass% is desirably shown by less than [;5mass%]. If;13mass% is exceeded in Bi**** of solder will be lostand workability supposes that it is bad. That isthese conditions are the soldering intensity at the time of targeting aluminumand viscosityand are not taken into consideration about the printed circuit board which consists of a Cu conductor. Although this presentation field is decided based on **** of the melting pointintensityand melting solderonly two samples are indicated by the example of Sn-Zn-Bi3 element systemthat data does not exist about **** of melting solderand determining the presentation of Sn-Zn-Bi has many ambiguous portions.
[0014]On the other handas for JP59-189096Athe solder which the remainder becomes [Zn] from Sn 3 - 20mass% 5 - 15mass% in Bi is proposed. This aims at the improving strength in connection of a wireand is not taken

as the object of connection of the printed circuit board which consists of a Cu conductor. In the case of Znless than [;5mass%] as a reason for deciding the range of this Zn (5 - 15mass%) and Bi (3 - 20mass%)the point which is insufficient strengthand the point which becomes weak with intensity increasing if an addition is increasedand melting temperature also risingand exceeding 15mass% are pointed out. In the case of Bi; if 20mass% is exceeded and solder will become weak is used. Although this presentation field is decided based on the melting point or adhesive strengththere is no desired value of the melting point and the examination process of the melting point using 3 element-system phase equilibrium constitutional diagram is not shown. Thereforethe presentation dependency of the melting point is not clear too.
[0015]
[Problem(s) to be Solved by the Invention]Since this invention mounts electronic partssuch as LSI and partsin the conventional glass epoxy board by high reliability using the solder for substitution of Sn-Pb eutectic crystal solder without including PbIt aims at being able to carry out a reflow below 220 **guaranteeing not less than 150 **and securing wettability and fully being able to carry out a reflow of it in weak fluxwith Sn system solder plating terminal composition of parts on Cu conductor.
[0016]For this reasonnot less than at least 150 ** of solidus temperature of the melting point is not less than (it can be equal to the 150 ** use in an elevated temperature) 160 ** desirablyLiquidus temperature made the technical problem a maximum of 195 ** or less of things desirably considered as 190 ** or less (soldering temperature becomes high and the thermal effect to a substrate and parts becomes largeas for making it high). Although some can be covered with metallizing on a terminal in wettability reservationin order to prevent the badness of the wetting by the physical properties of the material itselfit is necessary to press down the quantity of bad Zn of wetting to the minimum. Howeversince liquidus temperature does not fall greatly unless it can enter Znit is necessary to maintain balance with wetting and to decide a presentation. in Sn-Zn2 element system -- Sn -- Zn -- 9mass% -- although it becomes the minimum with a melting point of 199 ** in the state where it put innow the melting point is still high as mentioned aboveand wetting is too bad in a reflow which is 220 **.
[0017]That isin the solder which does not contain Pbi.e.the solder which consists of Sn-Zn-Bithe first purpose of this invention is to provide the presentation of the solder which can mount electronic partssuch as LSI and partsin organic insulating substratessuch as the conventional

glass epoxy boardby high reliability. A reflow can be carried out below 220 ** andspecificallyit is flux weak [guaranteeing not less than 150 **]. It is in fully securing wettability with Sn system solder plating terminal composition of parts on Cu conductorand providing the solder which can carry out a reflow.
[0018]The second purpose of this invention is to mount electronic partssuch as LSI and partsin organic insulating substratessuch as a glass epoxy boardby high reliability using the solder which does not contain Pb.
[0019]The third purpose of this invention is to provide the mounting article mounted in organic insulating substratessuch as a glass epoxy boardusing the solder which does not contain Pb.
[0020]
[Means for Solving the Problem]To achieve the above objectsthere is little influence on environment in Pb free solderThere was little toxicityit excelled in corrosion resistance and creep resistanceand melting point temperature could be loweredand a temperature gradient with liquidus temperature and solidus temperature was made smallreliability at the time of connection was raisedand an alloy which used as a base 3 element-system solder of Sn-Zn-Bi which can secure wettability further was examined as a candidate. As shown in drawing 1 until nowit is a grade which an outline of the melting point (liquidus temperature) understandsand details of a constitutional diagram of this 3 element-system solder are strange. For this reasonit is necessary to clarify relation between the melting point (solidus temperatureliquidus temperature) and a presentationrelationssuch as a presentationwettabilityphysical propertiesand a mechanical propertyetc. Thenit started with making a Sn-Zn-Bi3 element-system constitutional diagram.
[0021]And in order to attain said first purposein solder which consists of Zn-Bi-Snless than [more than 4mass%5mass%] and Bi were made less than more than 13mass%16mass%and the remainder was set to Sn for Zn. Or a weight (mass) % display of a presentation was expressed as coordinates (ZnBiSn)and it was considered as 3 element-system presentation of a Sn-Zn-Bi system of a presentation which is surrounded by A (616**)B (613**)C (5.512**)D (4.514**)and E (3.716**)and changes.
[0022]In a board mounting method using lead-free solder which consists of Zn-Bi-Sn in order to attain said second purposeSoldering paste which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass%16mass%and set the remainder to Sn by printing to an organic insulating substrate. Said soldering paste was

melted below at heat-resistant temperature of said organic insulating substrateand said organic insulating substrate and its mounted part were connected.
[0023]A mounted part carried in an organic insulating substrate and said organic insulating substrate in order to attain said third purposeSaid organic insulating substrate and said mounted part were used as a mounting article connected with solder which consists Zn of Zn-Bi-Sn which made less than more than 4mass%6mass% and Bi less than more than 13mass%16mass%and set the remainder to Sn.
[0024]Wettability was secured by using a paste made and crowded with a process in which the solder surface does not oxidize for wettability reservationand connecting by N_2 reflow and a vapor reflow.
[0025]
[Function]In ZnBi 4 - 6mass% Thus13 - 16mass%the remainder sets to Sn -- or the weight (mass) % display of a presentation -- coordinates (Zn.) By considering it as 3 element-system presentation of a Sn-Zn-Bi system of the presentation which displays by Bi and Snis surrounded by A (616**)B (613**)C (5.512**)D (4.514**)and E (3.716**)and changesThe characteristic which lowered liquidus temperatureand secured the mechanical reliability in the elevated temperature as solder for glass epoxy board connectionand was excellent in reflow nature (a temperature gradient with liquidus temperature and solidus temperature is lessened) is obtained. And the wettability to Cu board is secured and good mechanical properties are reconciled.
[0026]The reason which limited the solder presentation above is as follows.
[0027]To connectionit is desirable to lessen a temperature gradient with liquidus temperature and solidus temperature as much as possible. Becausenoisessuch as vibration at the time of conveyancecan be considered according to the cooling process of a reflow. For this reasonif a temperature gradient with liquidus temperature and solidus temperature is largesince solid phase and the time at the time of liquid phase coexistence are longthe probability that noisessuch as vibrationwill enter will become high. For this reasonit is easy to produce a connection fault and there is a possibility that a problem may appear in the reliability of a joint. The temperature gradient of liquidus temperature and solidus temperature has large Zn at less than 4mass%and connection at 220 ** or less is difficult. The above-mentioned temperature gradient becomes large more than 6mass%. According to the tensile test by Sn-xZn-15Bi (the amount x= 2 of Zn35 and 67mass%)in order to obtain solder twice [about] the tensile strength of a Sn-Pb

eutectic crystal and to obtain high intensity especially at the time of amount about 6 mass(es)% of Znthe amount of Zn is understood that about 6mass% is good. Scaling of solder becomes intenseif flux with a track record was used as electronic-parts solderingit becomes impossible to secure wettabilityso that there are many amounts of Znbut. Near amount of Zn 5mass%since about 85% of wetting (rate of a wetting flare of a solder ball) of pure Sn is still securableit is satisfactory. At less than 13mass%since liquidus temperature is not less than 194 **it becomes difficult to reflow connect Bi at 220 **. In Bisolidus temperature falls at 150 ** or less at more than 16mass%and the tensile strength in the elevated temperature of solder material falls. Thereforemargin reservation of the reliability in an elevated temperature becomes difficult. -In order to be able to be equal to a 55-150 ** temperature cycle accelerated testeven if low as solidus temperaturenot less than 160 ** of not less than 150 ** is desirably required.

[0028]If it is the solder of such a presentationsoldering without lead within the heat-resistant temperature of a glass epoxy board will be attainedThe solidus temperature the melting point of said solder That isnot less than at least 150 **It is desirably considered as not less than (it can be equal to the 150 ** use in an elevated temperature) 160 **Since the liquidus temperature considers it as 190 ** or less (soldering temperature becomes high andas for making it highthe thermal effect to a substrate and parts becomes large) desirablyit realizes a maximum of 195 ** or less of mounting substrates in the conventional reflow temperature of 220 **. The mounting article using lead-free solder will be provided also to a heat-resistant low glass epoxy board by such a mounting substrate being realizable.

[0029]

[Example]Hereafteran example explains this invention still in detail.

[0030]In the Sn-Zn-Bi3 element-system constitutional diagram of drawing 1only the relation between rough liquidus temperature and solidus temperature is known. It is a factor with liquidus temperature and solidus temperature important for solderingand when the yield of connection is relatedthe temperature gradient of liquidus temperature and solidus temperature is also an important factor. Thenit decided to investigate thoroughly the solidus temperature and liquidus temperature of the presentation extracted to the melting point region to need by DSC. Measurement was performed with the heating rate of 2 ** / min. The obtained DSC curve the shape in which the range by the side of the low temperature of an endothermic peak expands. Since it takes and solidus temperature is not strictly exact by the conventional method (let

temperature of the intersection of the tangent drawn towards the elevated-temperature side from the straight part before going into an endothermic peakand the tangent drawn towards the low temperature side from the endothermic peak be solidus temperature)The straight part of the DSC curve considered it as the temperature of the point which begins to change to a curve by an endothermic peak as the definition.

[0031]Drawing 2 expands the range near pure Sn of drawing 1and displays liquidus temperature and solidus temperature. According to thisit goes into the demand range in the range with little Bi to solidus temperaturebut since it turned out that it becomes 150 ** or less when the amount of Bi(s) became more than 13mass% and it became 160 ** or less and more than 16mass%it is predicted that the temperature gradient of liquidus temperature and solidus temperature becomes large. In this caseas for solidus temperaturesince it becomes impossible to take the margin of the reliability in an elevated temperature and becomes easy to produce the problem of a connection processit is desirable that it is not less than 160 **. Although liquidus temperature becomes low locally and it turns out in drawing 1 that the Sn-Zn eutectic crystal line of 2 yuan which makes the difference of solidus temperature and liquidus temperature small is extended with Sn-9Zn as the starting point to 3 yuan eutectic point Sn-4Zn-56Bi (melting point of 130 **)Since drawing 1 is roughthe exact position of the Sn-Zn eutectic crystal line (curve) of 2 yuan to which the two points are connected does not understand it. Thenin order to know thisit decided to measure minutely about the field shown at the amount 4 of Zn including the field the Sn-Zn eutectic crystal line of 2 yuan is indicated to be on drawing 1 - 6mass% the amount 10 of Bi(s) including the field where solidus temperature will be 160-170 ** - 14mass%. The result was shown in drawing 2. According to thisthe valley where the amount of Bi(s) will be 10 - 14mass%and Zn becomes low [liquidus temperature] at 5 - 6mass% of within the limits existsand it turns out that this is a Sn-Zn eutectic crystal line (drawing 2 thick line) of 2 yuan. That isin order to take as small the difference of solidus temperature and liquidus temperature as possibleit turns out that what is necessary is just to choose the presentation on this 2 yuan eutectic crystal line. Since the liquidus temperature of this 2 yuan becomes high rapidly in a presentation field with many amounts of Zn across a eutectic crystal lineit turns out that it is not practical as an object for electronic-parts connection. Howeverin order thatas for a eutectic crystal lineZn of 2 yuan may go into the field beyond 5mass% in the needed field used as the solidus temperature of not less than 150 **4.5 - 6mass% of the amount of Zn is desirable also in 4

- 6mass% of inside. Nextsince liquidus temperature needs to be 195 ** or lessit makes the amount of Bi(s) more than 12mass%. If solidus temperature is not less than 150 ** as stated previouslyin order to consider less than 16mass% and a margin and to consider it as not less than 160 **less than 13mass% of the amount of Bi(s) is desirable.
[0032]Drawing 3 plots the data which obtained the result of the constitutional diagram of drawing 2and it from the result analyzed still in detail. They are temperature-gradient deltaT of the liquidus temperature at the time of making the amount of Bi(s) 16mass% regularity 14mass% 13mass%respectivelyand solidus temperatureand a relation of the amount of Zn. the amount of Bi(s) -- the time of 13mass% and 14mass% -- Zn5.5mass% -- deltaT is the minimum in order. the time of the amount of Bi(s) being 16mass% -- Zn5mass% -- deltaT is the minimum in order. These results to 4 - 6mass% of Zn is desirable. Even if there are many amounts of Znsince deltaT increasesit is not desirable from a viewpoint of connection. [at least] It is not desirable on the problem of the reliability at the time of connection to maintain the coexistence region of a fluid and a solid long time at the time of cooling. Nextthe liquidus temperature to the amount of Zn is shown. It is desirable from a viewpoint of wettability to lower liquidus temperature as much as possible from constraints with a reflow temperature of a maximum of 220 **. It is made desirable in the viewpoint of wettability and the viscosity of a fluid to carry out a reflow at a temperature high 30-50 ** from the melting point experientially. Thereforein the case of 220 ** reflow temperaturemaximum liquidus temperature is 195 **. Drawing 4 is the liquidus temperature to the amount of Znwhen the amount of Bi(s) is considered as 14mass% regularity. whether the amount of Zn increases or it decreasesliquidus temperature rises -- the amount of Zn -- 5mass% -- it becomes the minimum in order. That isZn serves as a field which can lower liquidus temperature and can take a small temperature gradient with liquidus temperature and solidus temperature in 4 - 6mass% of the range.
[0033]Nextit wets wet with the amount of Znand a relation with a spread rate (evaluation of the wettability over oxidation of Zn) is shown in drawing 5. Since it wets wet at more than 6mass% and the rate of a flare approaches constant valueas an amount of Zn from a viewpoint of wettabilityless than 6mass% of the amount of Zn is desirable.
[0034]Connection resilience was examined. Drawing 6 shows the tensile strength to the amount of Znwhen the amount of Bi(s) is considered as 15mass% regularity. Tensile test conditions are room temperatures and were evaluated at the tension speed of 0.05 mm/min. Gauge length is 10

mm. The specimen was cast by a nitrogen atmosphere and cast was performed with the same cooling rate as reflow conditions. It produced by the electron discharge method so that heat might not be applied to a specimen. the amount of Zn -- 6mass% -- the strong maximum is shown in orderand at more than 6mass%if the tendency to fall rapidly is shown and the amount of Zn decreasesintensity will fall. Thereforethe range whose amount of Zn is 4 - 6mass% is considered to be an appropriate range.
[0035]The melting point (liquidus temperaturesolidus temperature) is decided by the combination of the amount of Znand the amount of Bi(s). Since wettability etc. are especially influenced greatly about the amount of Znvarious kinds of above-mentioned examination is needed. As the amount of Bi(s) is shown in drawing 7wettability is stable in the range with the wide amount of Bi(s). Thereforethe amount of Bi(s) has a large role of the melting point (liquidus temperaturesolidus temperature) adjustment in combination with the amount of Zn.
[0036]The detailed examination from the field of soldering nature is shown below. The reflow temperature of a maximum of 220 ** estimated the wettability of the solder to Cu terminal of a printed circuit board. evaluation changes a presentation for the wetting spread rate of a solder ball with a diameter [on Cu board] of 1 mm (Sn-5 Zn-xBi (x= 0101519222530)Sn-yZn-19Bi (y= 013457) measurement was carried outand the size performed.) The used flux is a rosin system containing 0.2mass% of chlorine. The value of the wetting spread rate was put on Table 1and showed drawing 5 and drawing 7 the result as above-mentioned. Wettability is fallingso that there are many amounts of Zn.
[0037]
[Table 1]

[0038]Similarlywhen the influence of the wettability by the amount of Bi(s) is investigatedby this systemit turns out that it hardly depends for wettability on the amount of Bi(s). It turns out that the solder ball near the composition range of a claim has secured the rate of a wetting flare of about 150% of an Sn-9Zn solder ball about 85% of pure Sn solder balls. Although it depended greatlyand wettability was near the composition range of a claim and was not more enough for the amount of Zn than thisit turned out that wetting required for connection is obtained. In order to lengthen the soldering paste in the composition range of a claim thinly and to supply it on a substrate by printing on the other handWhen an exhaust air reflow process is adoptedsolder particles are small in 10 micrometers and the number of diametersand

although there are few problems in respect of a wetting spreadsince a solder particle whole surface product serves as a big valuethere is a possibility that the particles by scaling of the particles at the time of a reflow may meltthe remainder may occurand the problem of an electrical property may occur. In order to have solved this problemit turned out that it is clearable by using N_2 reflow or a vapor reflow whose soldering is possiblepurging O_2. Since especially this solder did the firm oxide film when it was exposed to the atmosphere also by the instantwettability has been secured by the device pasted without exposing to the atmosphere. two kindsthe method which carries out a reflow of this paste using stronger fluxand is washed and to holdand the method which carries out a reflow using weaker fluxcarries out a reflow by an inert atmosphereand is not washed-- having inquired .

[0039]The presentation of a sample is changed in order to evaluate in a strong field (Sn-5 Zn-xBi (x= 01015171925) and a Sn-yZn-15Bi (y= 2356) room temperature tensile test were doneand shown in drawing 6.). According to itthe tensile strength of Sn-5 Zn-xBi is improving about 50% as compared with the time (two element systems) of x being 0mass%when x is 10 - 20mass% (three element systems). Since Bi dissolved and this caused solid solution hardening in (Sn) which serves as a matrix in a (Sn)+Zn phase ((Sn) expresses the solid solution of Sn base) at a room temperature by adding Bi and considering it as three element systemsit is considered. Thereforea pace of expansion decreases. It seems that weak (Bi) crystallized without the ability to dissolve in (Sn) will increaseand tensile strength will be reduced if the amount of Bi(s) is made to increase furthermore. On the other handalthough the tensile strength of Sn-yZn-15Bi serves as the maximum in the y= amount of Zn 5 neighborhoodAlthough this has a thick pure Zn needle crystal of the high intensity (about 12 kgf(s)/mm^2; Japan Institute of Metals metal data book P147) in a (Sn)+Zn phaseand becomes long with the increase in the amount of Zn and the (Sn) matrix is strengthenedThe compatibility of a needle crystal and a matrix falls as the size of a needle crystal becomes largeand it seems that it is because the effect of compound strengthening of a needle crystal and a matrix is lost. The value of the tensile strength is shown in Table 2.

[0040]

[Table 2]

[0041]It turned out that the tensile strength of Sn-(5-6) Zn-(10-20) Bi shows more than 9 kgf(s)/mm^2 and eutectic composition twice [about]

the value of Sn-Pb according to the two above-mentioned synergistic effects.
[0042]Although this invention targeted the glass epoxy boardit cannot be overemphasized that it can be used for other epoxy system boards and the heat-resistant board beyond itfor examplea glass polyimide substrateBT (glass cloth base material bismaleido triazine) boarda ceramic substrateetc.
[0043][The example of application to module board mounting] Drawing 8 (a) is an example of a power module mounting substrate at the time of joining the Cu heat sink plate 5 to the ceramic insulating substrates 4such as aluminum$_2$O$_3$ which carries the Si chip 3with the Sn-5Zn-13Bi solder 6. Drawing 8 (b) shows Cu heat sink plate which shows the Cu heat sink plate 5 which performed nickel plating 7and the Sn-5Zn-13Bi solder foil 6 rolled to 0.2-mm thicknessjoins both and is shown in drawing 8 (c) and which carried out preliminary soldering. Generally as for metallizing to a ceramic insulating substratethe composition of W-nickel-Au8 of nickel plating and Au plating thin on it is adopted as W conductor. In this caseby connecting the Si chip 3 and the ceramic insulating substrate 4 beforehand with the hot Sn-5mass%Sb solder 9 (melting point: 240 ** of liquid phase232 ** of solid phase)The 220 ** temperature hierarchy connection using Sn-5Zn-13Bi solder is possible without melting this Sn-5mass%Sb solder. As other solder material which connects the Si chip 3 which makes possible temperature hierarchy connection with Sn-5Zn-13Bi soldertemperature hierarchy connection is possible also for Au-20mass%Sn (melting point: 280 ** of liquid phase) similarly. The AlN board etc. which are excellent in heat leakage nature as an insulating substrate in addition to aluminum$_2$O$_3$ are used. nickel plating (about 0.2-micrometer Au plating or on nickel plating) is used on W or Mo metallizing film as metallizing material of these ceramic substrates. It is common to cover several micrometers nickel plating to Cu boardand to prevent and use scaling of Cu for it as a heat sink substrate. The same connection is possible by performing nickel plating similarly to heat sink materialssuch as WMoor other composite boards. Although soldering to Cu board directly is also possibleIt is also possible by performing nickel plating on giving 1-2 micrometers of Zn on Cuin order to maintain the intensity of an alloy layerand performing Sn plating on itor Cuand performing Ag plating on it etc. to prevent the strength deterioration in an interface. Since the bonding strength of this solder is highit is expectable to excel also in the creep resistance in an elevated temperature and a heat-resistant fatigability. Since Cu heat sink plate can be joined to an insulating substrate in strong flux when the semiconductor etc. are not carrieda zygote with few

voids is made. If temperature hierarchy connection is utilizedit is also possible to make contrary to the above the position which uses solder. Although supply of solder has common rolling foilthe method etc. which carry out paste printing are possible. The rolling nature of solder foil is comparatively goodand possible in the range of 0.1-0.2-mm thickness. In paste printingthe use as reserve solder is main.
[0044][The example of application to a surface mount] Although it is as having already described abovesoldering paste is used and QFP and a chip are described about the case where it connects with a printed circuit board by N_2 reflow. An object pitch is a 0.5-mm pitch and the particle diameter of a solder ball is around 50 micrometers. Cu pad -- pad width; -- it is 0.28 mm and Cu foil thickness is 18 micrometers. In order to prevent scaling by Znalso when making a pastethe creativity which does not expose a solder ball to the atmosphere directly was put. Thereforewhen it was among N_2 atmosphere with an oxygen density of about 100 ppm or vaporit turned out that the undersurface printed at least wets wet. In respect of wetting spread natureit is less than solder conventionally. Howeverflux a little stronger against securing sufficient wetting was usedand the paste of the washing type which carries out backwashing by water after a reflow was used.
[0045][The example of application to the surface mount of BGA] After pasting up the Si chip 3 on the organic group board 10the wire bond of drawing 9 is carried out with Au wire 11and it shows the example applied to connection of the BGA (Ball Grid Array) package which took resin molding 12. The Sn-5Zn-13Bi solder ball 13 with a diameter of 0.75 mm is madeand it arranges on the terminal of the organic group board 10and melts by stronger fluxand the ball 13 is formed on the terminal by the side of the glass epoxy board 14. A terminal pitch is 1.27 mmthe diameter of a substrate pad is 0.75 mmthe diameter of package terminals is 0.70 mmand terminal numbers are about 500 pins. The solder bump height after a reflow is about 0.6 mm. Unevenness at the tip of a ball of 500 pins was a maximum of 20 micrometers. If the flux 26 is applied on the glass epoxy board 14this BGA is carried and N_2 reflow is carried out at 220 **the high yield connection near 100% will be attained. Since the crevice between BGA and a substrate is largewashing of flux is easy. On the other handthe washing loess process of flux using low residue flux in consideration of the environmental problem is also possible. The flux loess method depending on few reduction nature of the volatile solvent with a carboxyl group is also possible. Connection on good conditions is possible by carrying out in N_2 reflow atmosphere so that it may not oxidize in this case at the time of a reflowperforming about

3 micrometers of nickel plating on Cu PATSUDO 15in order to use the terminal of a substrate that it is hard to oxidizeand also performing 0.1-micrometer Au plating on it. Flux loess connection is more certainly enabled by carrying out a surface treatment to scaling of a solder ballso that the surface may be licked by excimer laser etc. immediately before. Although the cause of the surface treatment effect by this excimer laser is unknownit is said that there is an effect it not only destroys a surface oxide filmbut carried out that it is hard to oxidize. As a method which connects BGA to a glass epoxy boardlike QFP mountingthe paste 16 is applied on the Cu pad 15 of a substrateand the method which carries and carries out a reflow of the BGA on it is also possible. When applying and carrying out a reflow of the pastereserve solder is turned on the pad side of a substrate. When carrying out a reflowit connects with soldersuch as a little Sn-Bi systems which are excellent in the wettability not only in the same presentation but 220 **and a Sn-Bi-Ag systemand connection with the Sn-5Zn-13Bi solder ball by the side of BGA is possible. Even if it fuses from an Sn-5Zn-13Bi solder ball being the main ingredientsin the melting pointit is seldom different from Sn-5Zn-13Bi solder.
[0046][The effect of trace element addition] The effect at the time of adding a little AgSb(s)Cu(s)and In(s) to Sn-5Zn-15Bi solder was examined. Ag and Cu are [as opposed to / especially / corrosion] the primary phases of Zn which is not desirable. (close to pure Zn of an ingredient) Since the corrosion of Zn was prevented by making a compoundit turned out that corrosion resistance is improvable. The addition of Ag can improve at 2% or less. The addition of Cu can improve at 1.5% or less. Howeverit turned out that addition has not influenced refining of Zn directly in Sb and In. Addition of In is useful for an improvement of wettabilityand Sb is useful for the mechanical-strength improvement.
[0047]Drawing 10 draws a line on 30 micrometers of wire sizes in Sn-5Zn-13Bi soldershows the connection type which enables connection of a 130-micrometer pitchand shows the process which carries out a wire bond directly on aluminum conductor of Si chip. (a) is a process which is sticking by pressure the solder which formed the ball by the capillary tube 17 on the aluminum conductor 18 (heat and an ultrasonic wave may be added). (b) is in the state which tore off the line in the place clamped and extracted and formed the solder terminal 21 after adhesion. (c) is in the state which sent out the solder line of fixed length at the tip of a capillary tube. If (d) is fused in an instant in an arc or laser 19 grade in an inert atmosphere or a reducing atmospherein the tip of a solder linethe spherical ball 20 will be formed in an operation of

surface tension. Drawing 11 around chip 1 the solder terminal 21. After performing leveling of the height of a solder vamp for the formed chipput the block 22 of a hardened type epoxy resin under a chip in the center beforehandposition a solder vamp for the Cu-nickel-Au terminal 23 of the organic group boards 14such as glass epoxyand heat crimping is carried out by an inert atmosphere. Flip chip bonding is carried out. Since resin does not arrive to a terminal where heat crimping is carried outmetal junction is possible. If the resin 25 is poured after junction and on the outskirts 27 of a chipin an operation of surface tensionit will be able to knead easily in the crevice between chip peripheriesand will cover. the used resin -- 500 to 1000 kgf/mm Young's modulus ^{2}and coefficient-of-thermal-expansion 15x10$^{\sim 6}$/**-35x10$^{\sim 6}$/** -- it has physical properties. High reliability mounting is enabled to a glass epoxy board etc. also with a large-sized chip by using this resin. In order to raise the junction nature of solder and Au for flux loess junctionit is effective to remove the oxide film formed in the solder surface by excimer laser etc. Although it connected with aluminum conductor of a chipa spherical solder vamp can be made by providing metallizing which wets a terminal area wet in solder by acting as a wetback of what carried out the wire bond in flux. Since this solder has small phase boundary potential with aluminumthere is the strong point by which difference electric corrosion is not generated easily. Since there is intensity also in drawing etc. and it is stickyit does not go outbut it can extend continuously.
[0048]
[Effect of the Invention]As mentioned abovethe Sn-Zn-Bi system solder of this inventionA harmful element is not included to environment like PbIt does not become a high cost but can solder to the glass epoxy board which is stabilized in resources and used from the former with reflow temperature equivalent to the conventional Sn-Pb eutectic crystal solder that it can supply with N_2 reflow device which is the conventional process. This solder has intensity as strong as about (nine to 10 kgf/mm tensile strength ^{2}) 2 times of a Sn-Pb eutectic crystaland it is excellent in high temperature strength-proof and creep resistance. Compared with the conventional Sn-Pb eutectic crystal solder also as a splice of electronic partsit has equivalent fatigue resistance.
[0049]Pb-free soldering (mounting) to organic insulating substratessuch as a glass-epoxy-resin board which was difficult until nowis realized.
[0050]Similarlyoffer of the mounting article mounted in organic insulating substratessuch as a glass-epoxy-resin boardusing Pb-free

solder is realized.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]publicly known Sn-Zn-Bi 3 element-system constitutional diagram (liquidus temperature)
[Drawing 2]The Sn-Zn-Bi3 element-system constitutional diagram near [which was clarified by thermometric analysis] pure Sn
[Drawing 3]The relation of a temperature gradient with the amount of Zn in a Sn-Zn-Bi systemand liquidus temperature and solidus temperature
[Drawing 4]The relation of the amount of Zn and liquidus temperature in a Sn-Zn-Bi system
[Drawing 5]It wets wet with the amount of Zn in a Sn-Zn-Bi systemand is a relation of the rate of a flare.
[Drawing 6]Relation between the amount of Zn in a Sn-Zn-Bi systemand tensile strength
[Drawing 7]It wets wet with the amount of Bi(s) in a Sn-Zn-Bi systemand is a relation of the rate of a flare.
[Drawing 8]The sectional view of a power module and the process of reserve solder are shown.
[Drawing 9]They are a sectional view of BGAand the expansion of a terminal area.
[Drawing 10]The section which shows a solder bump formation process method is shown.
[Drawing 11]The sectional view showing the method of mounting a solder vamp method is shown.
[Description of Notations]
1. Sn-Zn eutectic crystal line of 2 yuan
2. Sn-Zn-Bi eutectic structure appearance field of 3 yuan
3. Si chip 15.Cu PATSUDO
4. Ceramic insulating substrate 16. paste
5. Cu heat sink plate 17. capillary tube
6. Sn-5Zn-13Bi solder 18.aluminum conductor
7. nickel plating 19. arc or laser
8. W-nickel-Au 20. ball-like ball
9. Sn-5mass%Sb solder 21. solder terminal
10. Organic group board Block of 22. epoxy resin
11. Au wire 23.Cu-nickel-Au terminal
12. Resin molding 24. organic group board

13. Solder ball 25. resin
14. Glass epoxy board 26. flux
27. Chip circumference